

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.



AU9511686

(12) PATENT ABSTRACT (11) Document No. AU-A-11686/95
(19) AUSTRALIAN PATENT OFFICE

- (54) Title
ACROLEIN POLYMER
- (51)⁵ International Patent Classification(s)
C08F 116/34 A01N 035/02
- (21) Application No. : 11686/95 (22) Application Date : 10.02.95
- (30) Priority Data
- (31) Number (32) Date (33) Country
4404404 11.02.94 DE GERMANY
- (43) Publication Date : 24.08.95
- (71) Applicant(s)
DEGUSSA AKTIENGESELLSCHAFT
- (72) Inventor(s)
PETER WERLE; MATHIAS HOPP; OSWALD HELMLING; DIETRICH ARNTZ
- (74) Attorney or Agent
SPRUSON & FERGUSON, GPO Box 3898, SYDNEY NSW 2001
- (57)

The acrolein polymer is characterised by the physicochemical data:

$$\text{Weight average } \frac{\sum niMi^2}{\sum niMi} = Mw$$

wherein ni means number of mol and
Mi means molecular weight

Mw: 2000 - 6000 D

Carbonyl content: 0.5-5mol/kg of polymer

It is produced by simultaneously adding acrolein and catalyst to a reaction medium in a vessel in such a manner that the temperature of the reaction medium does not exceed 25°C and the pH value of the reaction medium is 10 to 11, the mixture is stirred on completion of addition and the acrolein polymer separated.

The acrolein polymer is used in biocidal agents.

SPRUSON & FERGUSON

Australia

Patents Act 1990

Notice Of Entitlement

I, John David O'Connor, of 31 Market Street, Sydney, New South Wales, 2000, Australia,
Patent Attorney for the Applicant/Nominated Person in respect of an application entitled:

Acrolein Polymer

state the following:-

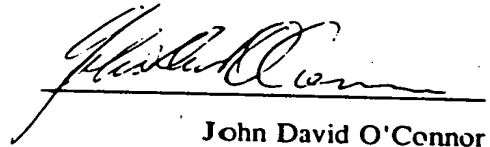
The Applicant/Nominated Person has entitlement from the actual inventors as follows:-

The Applicant/Nominated Person, by virtue of a Contract of Employment between the actual inventors as employees and the Applicant/Nominated Person as employer, is a person which would be entitled to have the patent assigned to it if a patent were granted on an application made by the actual inventors.

The Applicant/Nominated Person is the applicant of the basic application listed on the Patent Request.

The basic application listed on the Patent Request is the first application made in a Convention Country in respect of the invention.

Dated 5 January 1995



John David O'Connor

AUSTRALIA

SPRUSON & FERGUSON

PATENTS ACT 1990

PATENT REQUEST: STANDARD PATENT

I/We, the Applicant(s)/Nominated Person(s) specified below, request I/We be granted a patent for the invention disclosed in the accompanying standard complete specification.

[70,71] Applicant(s)/Nominated Person(s):

Degussa Aktiengesellschaft, incorporated in Germany, of 9,
Weissfrauenstrasse, D-6000 Frankfurt am Main, GERMANY

[54] Invention Title:

Acrolein Polymer

[72] Inventor(s):

Peter Werle, Mathias Hopp, Oswald Helmling and Dietrich Arntz

[74] Address for service in Australia:

Spruson & Ferguson, Patent Attorneys
Level 33 St Martins Tower
31 Market Street
Sydney New South Wales Australia (Code SF)

[31] Appl'n No(s):

P44 04 404.6

Details of Basic Application(s):

[33] Country:

DE

[32] Application Date:

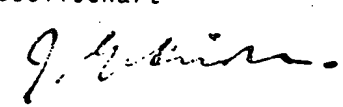
11 February 1994

Basic Applicant(s): Degussa Aktiengesellschaft

DATED this NINTH day of FEBRUARY 1995

Degussa Aktiengesellschaft

By:


Registered Patent Attorney

IRN: 290661

INSTR CODE: 53300

S 053116 100295

Acrolein polymer

This invention relates to an acrolein polymer, to a process for the production thereof, to a process for the preservation of materials using the acrolein polymer and to a biocidal agent which contains the acrolein polymer.

It is known to use monomeric acrolein (2-propenal) as a highly effective biocide in water systems against unwanted algal and plant growth. It may also be used to combat sulphate-reducing bacteria in petroleum exploration.

Because of its high reactivity, no further applications for the biocidal action of monomeric acrolein have yet been found. Due to its tendency when incorrectly handled to spontaneously and sometimes explosively polymerise, particular safety precautions are required for handling. It is highly irritant to the respiratory tract and eyes. Even when stabilised, acrolein may be stored for only a limited period.

It is known to use copolymers of acrolein with formaldehyde produced by condensation of acrolein and formaldehyde in a molar ratio of between 1:1 and 1:10 in the presence of a basic catalyst as biocides for aqueous systems (DE-B 32 05 487). The known copolymer of acrolein with formaldehyde has the disadvantage that it contains approximately 15% formaldehyde.

It is known to use acrolein homopolymers as biocides (EP-A 0 339 044). Polymerisation is predominantly performed by free-radical or ionic means using a sodium hydroxide solution.

Disadvantageously, free-radically polymerised homopolymers of acrolein are virtually insoluble in organic media or water and exhibit only very low biological activity in the form of an aqueous suspension. An aqueous suspension of the anionically polymerised acrolein described in example 1b of EP-A 0 339 044 also exhibits only inadequate activity against microorganisms.

For toxicological reasons, the described solution in methyl alcohol is not suitable for the production of products which may be handled. It also exhibits only moderate biocidal activity.

The process described in EP-A 0 339 044 of adding a catalyst to an acrolein solution cannot be performed industrially due to the highly exothermic reaction which is spontaneously initiated.

There is thus an object of providing an acrolein polymer which is toxicologically harmless and safe and exhibits elevated biocidal activity.

The present invention provides an acrolein polymer, which is characterised in that it has the following physicochemical parameters:

$$\text{Weight average } \frac{\sum n_i M_i^2}{\sum n_i M_i} = M_w$$

wherein n_i means number of mol and

M_i means molecular weight

M_w : 2000 - 6000 D

Carbonyl content: 0.5-5mol/kg of polymer

The present invention also provides a process for the production of the acrolein polymer, which process is characterised in that acrolein and catalyst are simultaneously added to a reaction medium in a vessel in such a manner that the temperature of the reaction medium does not exceed 25°C and the pH value of the reaction medium is 10 to 11, the mixture is stirred on completion of addition and the acrolein polymer separated.

In a preferred embodiment of the invention, water may be used as the reaction medium. An aqueous sodium hydroxide solution with a concentration of 0.01 to 10mol/L may be used as the catalyst. The temperature of the reaction medium may preferably be 20 to 25°C. The ratio of acrolein to catalyst may be 1:0.0001 to 1:0.05. The stirring time may be 1 to 3 hours, preferably 1 to 2.5 hours.

The solid may then be isolated from the resultant aqueous polyacrolein dispersion with a content of approximately 5 to approximately 30% at acceptable space-time yields if the pH is adjusted to the required range during the reaction. The polymer may readily be centrifuged in centrifuges of a conventional design and any residual acrolein may be eliminated from it by careful washing with water.

The still moist product discharged from the centrifuge, with a water content of approximately 35%, may readily be dissolved at 40 to 50°C within a short time in many polyhydric alcohols, such as propylene glycol, butylene glycol as well as glycols of the general formula $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$. Ethylene glycol and propylene glycol and the oligomers or ethers thereof are preferably used. The resultant solutions may have a polymer content of up to 30 wt%. They are clear, colourless or slightly yellow in colour. These solutions in $(\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H})$ are furthermore non-toxic, virtually odourless and constitute effective biocides.

Dipolar aprotic solvents, such as acetone, dimethyl sulfoxide, methylpyrrolidone, dimethylformamide, tetramethylurea may also constitute good solvents for the polymer.

When used in many areas, such as the preservation of dye dispersions, glues, textile auxiliaries, wax emulsions, wood protection lacquers and many others, these solutions may be homogeneously distributed by stirring.

It is also technically possible to convert the moist centrifuged product into a dry biocidally active powder, by using a disk drier preferably operated under a vacuum. Due to the low bed depth on the individual disks and careful movement by the raking arm, a very fine product may successfully be obtained. The drier is operated at temperatures of 20 to 50°C under a pressure of 1 to 100mbar.

Using a fluidised bed drier has been found to be another method of resolving the drying problem. Due to the elevated air throughput and vigorous mechanical friction of the individual particles of the product against each other, this method

yields an exceptionally finely divided powder which may be directly packed without further grinding.

In fluidised bed drying, it has been found to be advantageous to use a temperature program, wherein drying is initially started at a low temperature which is raised in stages. Drying is preferably begun at room temperature and the drying temperature is increased to up to 75°C. The polymer obtained using this drying process is a slightly yellow powder with a primary particle size of a few micrometres.

It is possible to use the acrolein polymer according to the invention as a preservative or biocide by direct incorporation, but the use of solutions in polyhydric alcohols of the type described above may here too be advantageous. When these solutions are poured into aqueous media, the polymer precipitates, which in the event of inadequate homogenisation may lead to a loss of biocidal activity.

It has surprisingly been found that by adding a small quantity of an inorganic or organic base to the alcoholic solutions it is possible to obtain water-dilutable or at least microdisperse systems with only a weak Tyndall effect. 0.05 to 0.1 mol of base may be used for 1kg of a 10 wt% solution of the polymer. An aqueous solution of sodium hydroxide is customarily used. Na-alkylates may, however, also be used. In addition to improved solubility, a distinct increase in disinfective action has also been found in short-term testing. The solutions may thus be stated to be activated by the hydroxyl ions. This property of the polyacrolein depends in a surprising and unpredictable manner upon the drying conditions. Products which have been dried at room temperature or $\leq 60^{\circ}\text{C}$ and optionally ground do not exhibit the solubilising effect due to the addition of a base. Only those preparations dried using the process according to the invention with a strong air current at final temperatures of $> 60^{\circ}\text{C}$, preferably at 75°C , are alkali-soluble.

The present invention also provides a process for the preservation of materials, which is characterised in that the acrolein polymer according to the invention is added.

The acrolein polymer according to the invention may, in particular, be added to the following materials: plastic dispersions, anti-fungal treatment solutions for wood, cladding and walls, wall paints, dye pastes and the like, sealing compounds, distempers, wood protection lacquers, adhesive emulsions, skin and leather glues, bone glues, starch glues, casein glues, dextrin adhesives, salted skins, pickling solutions, dried skins, tanning liquor, moist chromium leather, finished leather, spinning baths, wax emulsions, wax raw materials, textile finish (anti-fungal), textile dressings, paper/paperboard (anti-fungal), PVC coating (anti-fungal), drilling and cutting oils (diluted), drilling and cutting oils (concentrated), wood

preservatives, cellulose fibres (rotproofing agent), grouting cement, marine paints, liquid cleansers.

The acrolein polymer according to the invention may here be added to the materials in quantities of 0.01 to 0.3wt%.

5 The present invention also provides a biocidal agent which contains the acrolein polymer according to the invention. The biocidal agent may here contain the acrolein polymer according to the invention dissolved in a polyhydric alcohol, for example ethylene glycol (for example as a 10% solution). The biocidal agent may additionally contain an oxidising agent, such as H_2O_2 or peracetic acid and
10 optionally an alkali metal hydroxide, such as NaOH.

In another embodiment of the invention, the biocidal agent may contain an inorganic or organic base, such as for example NaOH or sodium alkylates (for example sodium methylate). The biocidal agent may contain the acrolein polymer according to the invention in a 20% dispersion in water.

15 In predominantly aqueous systems and in the event of inadequate mixing during incorporation, the dissolved polymer may precipitate in coarse particles and so give rise to reduced biocidal activity.

It has now been found that the polymer solutions containing glycol may be modified by treatment with small quantities of oxidising agents, such as hydrogen
20 peroxide or peracetic acid, with, optionally, subsequent addition of sodium hydroxide solution in such a manner that water-soluble or microdisperse systems are produced which do not exhibit the possible disadvantages caused by precipitation. The added quantity of oxidising agents, used in a 10 wt% polymer solution containing 100 g of solid polymer, may be 0.1 mol to 0.4 mol, preferably
25 0.2 mol to 0.3 mol of pure oxidising agent. The optionally added base solution is preferably used in quantities of 0.05 to 0.1 mol (as NaOH).

Examples

Example 1 (comparative example)

Example 1b according to EP-A 0 339 044 is replicated and the resultant dry
30 polyacrolein is dissolved in methanol (10% active ingredient content). A portion of the solution is evaporated and redissolved in methanol (c/f. EP-A 0 399 044, example 1a):

The process described in EP-A 0 339 044 is ruled out for industrial use on safety grounds. If, in contrast, the catalyst, in general an aqueous inorganic base
35 or a basic amine, is placed in the reaction vessel and the acrolein is added to it with vigorous external cooling in such a manner that the temperature in the reaction vessel does not exceed 25°C, colourless to slightly yellow precipitates are obtained which are only sparingly or incompletely soluble in the solvents according to the

invention. Insoluble fractions of polymer remain even at elevated temperatures (80°C). Exposure to elevated temperatures moreover causes undesirable discolouration of these solutions.

Example 2 (according to the invention)

330mL of water and 2.0mL of 1N NaOH are introduced into the reaction vessel and 120mL of acrolein and 6.8mL of 1N NaOH diluted with 60mL of water are steadily apportioned over the course of approximately 30 minutes with cooling to 5 to 20°C. The mixture is stirred for a further 1 hour at room temperature, the solid polymer separated, washed carefully with water and the polymer stirred into 700g of ethylene glycol heated to 45 to 50°C. After approximately 30 to 60 minutes, a light yellow, clear polymer solution with an active ingredient content of 10% is obtained. When this solution is poured into water, a heavy precipitate is formed.

The polymer (dried under vacuum at room temperature after separation) has a carboxyl content of 0.7mol/kg and a weight average of $M_w=3500D$.

Example 3

100g of a polyacrolein solution produced according to example 2 are combined at 20 to 25°C with 4.5mL of a 30wt% H_2O_2 solution and heated to 70 to 75°C. The solution is held at this temperature for 1 to 2 hours. When such a solution is poured into water, only slight turbidity is now visible. Post-oxidation with H_2O_2 thus leads to improved solubility in aqueous systems.

Example 4

125L of water are introduced into a reaction vessel and combined with 5L of a 1% NaOH solution. The solution is cooled to +5°C. 25L of acrolein and 5L of 1% NaOH solution are added in such a manner that the internal temperature does not rise above +25°C. The reaction mixture is stirred for a further 2 hours and then centrifuged. The solid is washed and cooled in the centrifuge.

24kg of moist powder are obtained which are dried in two batches in a fluidised bed dryer using the following program:

1h	25°C
1h	35°C
3h	75°C.

A total of 15kg of dry polymer are obtained with a carbonyl content of 2.2mol/kg and a weight average M_w of 4000D.

Example 5

A polymer produced according to example 4 is dissolved in ethylene glycol with heating and 100g of this 10% solution are combined with 200mg of NaOH

(dissolved in a little water) or with 300mg of solid NaOCH_3 . While the solution which had not been treated with alkali exhibited heavy precipitation of polymeric acrolein when poured into water, the solution treated with OH^- exhibited only slight turbidity. This means that solubility in water is improved by the addition of OH^- ions.

The microbicidal activity of the resultant preparation is determined using the so-called "time-kill-test" (TKT). In this test, which was performed following the recommendations of the American Petroleum Institute (API, RP 38, 2nd ed., Dec. 1965), a highly concentrated microbial suspension (microbial count 10^6 to 10^8) is combined with the desired quantity of biocide and incubated for 24 hours at 25°C . The suspension is then inactivated and a geometric dilution series of up to 6 is prepared; one 1mL of each dilution is mixed with 10mL of nutrient agar on plates and incubated for 48 hours at 37°C . The kill rate is calculated by counting the number of colonies.

The results are evaluated as follows:

The arithmetic mean of 2 values (two determinations) is calculated. The microbial reduction value KR_t per unit time in the TKT (24 h), also known as the rating value, is calculated using the following equation:

$$KR_t = \log \text{CFU}_{(\text{control})} - \log \text{CFU}_{(D)}$$

$\text{CFU}_{(\text{control})}$ = the number of CFU/mL without the action of the preparation (also known as the blank sample)

$\text{CFU}_{(D)}$ = the number of CFU/mL after the action of the preparation.

Good activity entails achieving reductions of at least 5 log increments.

Type of microbe: *Pseudomonas aeruginosa* ATCC 15442

Example n°	Temp.	pH	Time [h]	Conc. [ppm]	KR_t
1 (comparison)	25	6.5	24	500	2.8
1a	25	6.5	24	500	5.8
2	25	6.5	24	500	> 7.4
3	25	6.5	24	500	> 7.4
4	25	6.5	24	500	> 7.4
	25	6.5	24	200	3.0
5	25	6.5	24	200	> 7.4

The claims defining the invention are as follows:

1. Acrolein polymer which is characterised in that it has the following physicochemical parameters:

$$\text{Weight average } \frac{\sum n_i M_i^2}{\sum n_i M_i} = M_w$$

5 wherein n_i means number of mol and

M_i means molecular weight

M_w : 2000 - 6000D

Carbonyl content: 0.5-5mol/kg of polymer

2. An acrolein polymer, substantially as hereinbefore described with
10 reference to any one of the examples but excluding the comparative examples.

3. Process for the production of the acrolein polymer according to claim 1, which process is characterised in that acrolein and catalyst are simultaneously added to a reaction medium in a vessel in such a manner that the temperature of the reaction medium does not exceed 25°C and the pH value of the reaction medium is
15 10 to 11, the mixture is stirred on completion of addition and the acrolein polymer separated.

4. A process for the production of an acrolein polymer, substantially as hereinbefore described with reference to any one of the examples but excluding the comparative examples.

20 5. An acrolein polymer produced by the process of claim 3 or claim 4.

6. Process for the preservation of materials, which is characterised in that the acrolein polymer according to any one of claims 1, 2 or 4, is added to these materials.

7. Preservation process according to claim 5, characterised in that the
25 acrolein polymer is added to one or more of the following materials: plastic dispersions, anti-fungal treatment solutions for wood, cladding and walls, wall paints, dye pastes and the like, sealing compounds, distempers, wood protection lacquers, adhesive emulsions, skin and leather glues, bone glues, starch glues, casein glues, dextrin adhesives, salted skins, pickling solutions, dried skins,
30 tanning liquor, moist chromium leather, finished leather, spinning baths, wax emulsions, wax raw materials, textile finish (anti-fungal), textile dressings, paper/paperboard (anti-fungal), PVC coating (anti-fungal), drilling and cutting oils (diluted), drilling and cutting oils (concentrated), wood preservative, cellulose fibres (rotproofing agent), grouting cement, marine paints, liquid cleansers.

35 8. Biocidal agent characterised in that it contains acrolein polymer according to any one of claims 1, 2 or 4, together with a carrier.

9. Biocidal agent according to claim 8, characterised in that the acrolein polymer is dissolved in a polyhydric alcohol.

10. Biocidal agent according to claim 8 or claim 9, characterised in that it contains an oxidising agent and optionally sodium hydroxide solution.

11. Biocidal agent according to claim 8 or claim 9, characterised in that it contains an inorganic or organic base.

5

Dated 21 December, 1994
Degussa Aktiengesellschaft

Patent Attorneys for the Applicant/Nominated Person
SPRUSON & FERGUSON

Acrolein Polymer

Abstract

The acrolein polymer is characterised by the physicochemical data:

$$\text{Weight average } \frac{\sum n_i M_i^2}{\sum n_i M_i} = M_w$$

5 wherein n_i means number of mol and

M_i means molecular weight

Mw: 2000 - 6000 D

Carbonyl content: 0.5-5mol/kg of polymer

10 It is produced by simultaneously adding acrolein and catalyst to a reaction medium in a vessel in such a manner that the temperature of the reaction medium does not exceed 25°C and the pH value of the reaction medium is 10 to 11, the mixture is stirred on completion of addition and the acrolein polymer separated.

The acrolein polymer is used in biocidal agents.